# Photoabsorption cross sections of two-electron atoms by the coordinate rotation method: Application to $H^-$ and several states of He*

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The coordinate rotation method, recently extended by us to treat photoabsorption processes, is used to obtain photoabsorption cross sections for several two-electron atoms. The calculations are performed using standard configuration–interaction methods; the need for atomic continuum wavefunctions is completely avoided in this approach. We have computed the photodetachment cross section of $H^-$ and photoionization cross sections for He in its ground and $2\,^1S$ states. In all cases, the computed cross sections agree well with results obtained by numerical integration and with available experimental data.

## I. INTRODUCTION

In a previous paper,[1] Rescigno and McKoy outlined a method for computing atomic and molecular photoabsorption cross sections from a discrete basis-set expansion. We took advantage of the analytic properties of the Hamiltonian under a transformation that rotates all its coordinates by a complex phase factor and used these properties to derive an expression for the photoabsorption cross section at physical energies that could be evaluated using discrete, square-integrable basis functions exclusively. The method was illustrated by application to the model problem of atomic hydrogen.

While a number of other methods for constructing the photoabsorption profile of atoms or molecules from the results of a bound state calculation have been proposed,[2–4] the present technique is significant in that it allows the calculation to be performed directly at the physical energies of interest and relies on no secondary procedure to construct the cross section. In contrast to other $L^2$ calculations, the method employed here does not require calculations to be done at complex photon energies[2] nor does it involve the extraction of photoabsorption profiles from a moment analysis.[3] While we do work with complex eigenvalues, these appear unambiguously as the eigenvalues of a complex Hamiltonian and are not constructed by the addition of first order lifetimes to the results of an ordinary bound state calculation.[4]

In this paper, we apply the method of rotated coordinates to study the photoabsorption of several two-electron atoms. The method of configuration interaction is used to obtain photodetachment cross sections for the negative hydrogen ion as well as photoionization cross sections for helium in both its ground and $2\,^1S$ states. The methods used in the calculations presented here are standard bound state computational techniques. No new interaction matrix elements are required in constructing the Hamiltonian, and the numerical complications introduced by complex coordinates are minimal. These calculations are far more efficient than the direct solution of the differential equations for the atomic continuum wavefunctions. Furthermore, the formalism of rotated coordinates is easily extendable to the computation of molecular photoionization cross sections, where the difficulty of numerical integration of the continuum differential equations is greatly escalated.

In the following section, the theory is briefly reviewed. Section III discusses the numerical procedures used to obtain the cross sections, and Sec. IV presents our results. We conclude with a brief discussion in Sec. V.

## II. THEORY

The application of the coordinate rotation method to the computation of photoabsorption cross sections has been discussed previously in Ref. 1 and thus only a brief summary will be given here.

We treat the time-dependent Schrödinger equation using first-order perturbation theory and the semiclassical description of the radiation field. This yields the equation for the first-order wavefunction $\psi^{\pm}(r)$,[5]

$$[H(r) - E_0 \pm \omega]\psi^{\pm}(r) = \mu\psi_0(r) \,, \tag{1}$$

where $\omega$ is the photon frequency, $\psi_0(r)$ and $E_0$ are the unperturbed (not necessarily ground state) wavefunction and energy, and where the set of all electronic coordinates has been denoted by $r$. The dipole operator $\mu$ for photon polarization $\hat{e}$ is

$$\mu = \sum_i \hat{e} \cdot \mathbf{r}_i \,. \tag{2}$$

For the purpose of studying photoabsorption, it suffices to consider only the negative frequency component of the polarizability, which is given by[5]

$$\alpha^-(\omega) = \langle \psi_0 | \mu | \psi^- \rangle \,. \tag{3}$$

The photoabsorption cross section is related to the imaginary part of $\alpha^-(\omega)$ through the equation,

$$\sigma(\omega) = (4\pi\omega/c)\,\mathrm{Im}[\alpha^-(\omega)] \,. \tag{4}$$

In the method of rotated coordinates,[6] a contour distortion is performed in evaluating the matrix element of Eq. (3), so that the coordinate space radial integrations are carried out along the rotated paths defined by $\theta = e^{i\varphi}$, $\varphi > 0$.[7] The integral that results from this trans-

  

formation requires the function $\psi^-(r\theta)$, which we obtain by performing the transformation $r \to r\theta$ in Eq. (1),

$$[H(r\theta) - E_0 - \omega]\psi^-(r\theta) = \mu(r\theta)\psi_0(r\theta) \ . \tag{5}$$

The fact that $\psi_0(r)$ is a bound state assures that a range of $\varphi$ can be found such that $\psi_0(r\theta)$ still decreases exponentially. This condition along with the properties of the rotated Hamiltonian insure that $\psi^-(r\theta)$ is also a square-integrable function.[6] We use these properties of Eq. (5) to approximate $\psi^-(r\theta)$ by forming a matrix representation of the inverse of the operator $[H(r\theta) - E_0 - \omega]$ in a basis set of square-integrable functions. As discussed in Ref. 1, this representation is meaningful for all real values of $\omega$ and converges as the basis set is increased. The expression we arrive at for $\alpha^-(\omega)$ for an $N$ electron system is[1]

$$\alpha_\theta^-(\omega) = \sum_i \frac{\theta^{3N}\int\psi_0(r\theta)\mu(r\theta)\psi_i(r)d^3r \cdot \int\psi_i^*(r)\mu(r\theta)\psi_0(r\theta)d^3r}{E_i - E_0 - \omega} \ , \tag{6}$$

where $\psi_0(r\theta)$ is the unperturbed wavefunction evaluated at $r\theta$, and $E_i$ and $\psi_i$ are the complex matrix eigenvalues and eigenvectors of the (non-Hermitian) Hamiltonian $H(r\theta)$. The complex diagonalizations needed in this work were carried out using a routine obtained from the California Institute of Technology computer program library entitled ALLMAT/Arbitrary Complex Matrix Eigensystem Solver, which is a FORTRAN-coded, revised version of the IBM Share Program 3441.

Recent work on resonances in electron scattering using the rotated coordinate method has shown that there are discrete complex eigenvalues of $H(r\theta)$ which correspond to autoionizing states of the system.[8] If the basis set used to obtain $\alpha_\theta^-(\omega)$ is adequate to describe these states, then certain of the $E_i$'s will have small imaginary parts and appear as resonances in the photoabsorption cross sections. The behavior of these eigenvalues $E_i$ as a function of rotation angle is characteristically very different from the other eigenvalues of $H(r\theta)$.[8] The method of rotated coordinates, then, allows for the straightforward description of both resonant and nonresonant photoabsorption using only bound-state techniques.

## III. COMPUTATIONAL

The most straightforward, readily applicable technique for studying the wavefunctions of a two-electron system is the method of configuration interaction. In these calculations, the configurations were constructed from orthonormal one-electron atomic orbitals of general form

$$\varphi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \varphi) \ , \tag{7}$$

where the radial functions are linear combinations of Slater-type orbitals,

$$\{\alpha_{nl}^{n+l+3/2}/\sqrt{[2(n+l+1)]!}\}\, r^{n+l}e^{-\alpha_{nl}r}, \ n = (0, 1, \ldots) \ .$$

In this work, a matrix representation of the appropriate Hamiltonian was formed using all symmetry-adapted two-electron configurations for a specified value of total $L$ that could be constructed from a given set of Slater-type orbitals.

The initial atomic state was found by solving for the lowest (or, in the case of $2^1S$ He, the second lowest) singlet eigenvalue and corresponding eigenvector of the *real* Hamiltonian for total $L = 0$. In evaluating $\alpha_\theta^-(\omega)$ through Eq. (6), $\psi_0(r\theta)$ is found by simply evaluating this initial state eigenfunction at $r\theta$. Thus, $\psi_0(r\theta)$ is given as a linear combination (real coefficients) of products of *rotated* Slater orbitals.

The final states, $\Psi_i$, of Eq. (6) were found by diagonalizing the *rotated* Hamiltonian in the set of all symmetry adapted, two-electron configurations that could be constructed for $L = 1$. (Note that matrix elements of the rotated Hamiltonian are trivially obtained by multiplying the real kinetic energy matrix elements by $\theta^{-2}$ and the coulomb matrix elements by $\theta^{-1}$.)[8] Thus, the $\psi_i$ are all expressed as linear combinations (complex coefficients) of products of real Slater orbitals.

Some care is needed in evaluating the matrix elements of the rotated dipole operator that appear in Eq. (6). We note that these will be expressed as products of one-electron matrix elements and overlaps between real and complex basis orbitals. It is important to note that the overlap matrix will be nondiagonal even if the same basis functions are used to form both $\psi_0$ and the $\psi_i$. This is so because the orbitals referring to $\psi_0(r\theta)$ are evaluated at rotated coordinates, while those referring to $\psi_i$ are not.[1]

It is not necessary to actually diagonalize the $L = 1$ Hamiltonian matrix in order to construct the polarizability. When large sets of basis functions are being used, it may in fact be simpler to solve for $\alpha_\theta^-(\omega)$ by inverting the matrix $[H(r\theta) - E_0 - \omega]$ for each value of $\omega$ desired. This was the procedure that we followed in performing the calculations on $H^-$.

## IV. RESULTS

### A. The negative hydrogen ion

The photodetachment cross section of the negative hydrogen ion provides a useful test for examining the convergence of the coordinate rotation procedure since the detachment cross section is sensitive to the long-

TABLE I. Basis functions used to compute the $H^-$ ground state.

| $n^a$ | $l^a$ | $\alpha^a$ |
|---|---|---|
| 0 | 0 | 2.0 |
| 0 | 0 | 1.111 |
| 0 | 0 | 0.617 |
| 0 | 0 | 0.342 |
| 0 | 0 | 0.190 |
| 0 | 0 | 0.106 |
| 0 | 0 | 0.059 |
| 0 | 1 | 2.0 |
| 0 | 1 | 1.0 |
| 0 | 1 | 0.5 |
| 0 | 1 | 0.25 |
| 0 | 1 | 0.125 |

$E_0 = -0.5263$ a.u.

[a] $n$, $l$, and $\alpha$ refer to the parameters in radial Slater functions of the form $r^{n+l}e^{-\alpha r}$.

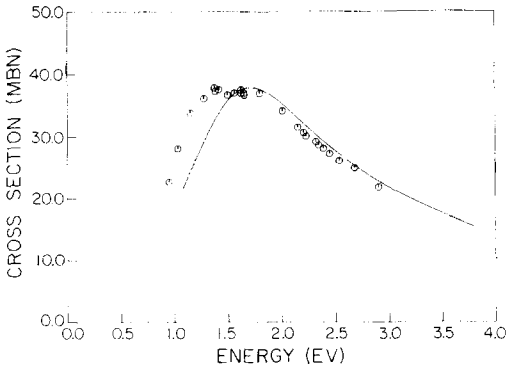


FIG. 1. Comparison of calculated photodetachment cross section of $H^-$ with the experimental results of Smith and Burch (⊙).[13] The relative experimental points have been normalized so that the maximum coincides with the computed value.

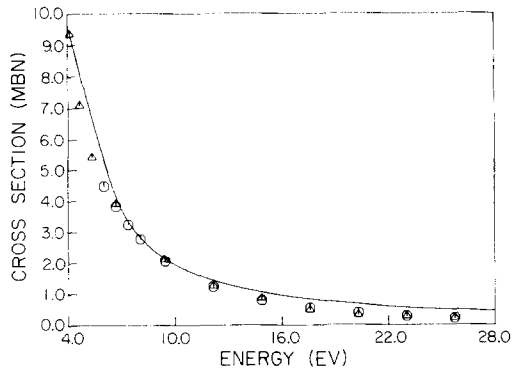


FIG. 3. Comparison of the calculated photoionization cross section of the $2\,^1S$ He atom with the theoretical results of Norcross (△)[20] and Jacobs (⊙).[21]

range tail of the diffuse ground-state wavefunction.[9] Moreover, the stability of the $H^-$ ion is due to correlation effects. Although the diffuse character of $H^-$ also allows one to derive highly accurate but simple formulas for the cross section in the asymptotic limit,[9,10] we have made no use of such simplifying procedures in our calculations.

In computing the ground state wavefunction of $H^-$, we carried out a full configuration interaction, CI, using $7s$- and $5p$-type Slater functions, whose orbital exponents are given in Table I. This calculation produced a ground-state energy of $-0.5263$ a.u., which is to be compared with the "exact" value of $-0.5277$ a.u. obtained by Pekeris.[11] An $88\times88$ matrix representation of $H(r\theta)$ was obtained by performing a CI on the rotated $L=1$ Hamiltonian using $6s$-, $8p$- and $5d$-type Slater functions. These functions were chosen by fixing the orbital exponents and varying $n$ in Slater functions of the form $r^{n+l}e^{-\alpha r}$. The values chosen for $\alpha$ were 1.0, 1.2, and 1.6 for the $s$-, $p$-, and $d$-type Slaters respectively; a similar choice has been used successfully by one of the authors in the related $e^- - H$ atom scattering problem.[12] For all the results to be reported in this work, the rotation angle was set at 20°. Clearly, very small values of rotation angle should be avoided, since the expansion of Eq. (6) could then be nearly singular. The particular choice of 20° was made on the basis of our earlier work on atomic hydrogen.[1]

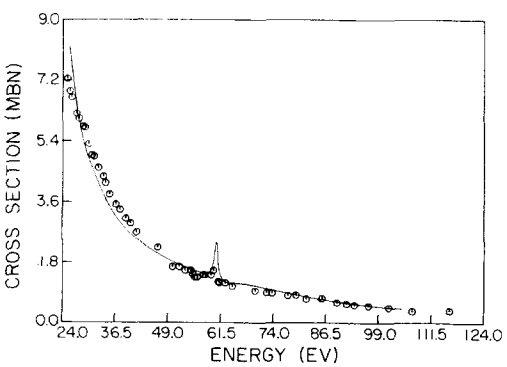


FIG. 2. Comparison of the calculated photoionization cross section of the ground-state He atom with the experimental points of Samson (⊙).[16]

Our results for the photodetachment cross section of $H^-$ are shown in Fig. 1 along with the experimental results of Smith and Burch.[13] Since the experimental points measure relative probabilities, they have been normalized so that the maximum coincides with our computed value. Our results are seen to be in good agreement with experiment except for the low-energy region near threshold where the cross section is apparently very sensitive to the details of the $H^-$ ground-state wavefunction. Slow convergence of the cross section near threshold is found even when explicitly correlated functions of the Hylleras type are employed as an expansion basis.[14]

### B. The ground-state helium atom

The helium ground-state wavefunction was obtained as a linear combination of the twelve configurations obtained from a basis of $3s$- and $3p$-Slater orbitals. The orbital exponents were chosen to be 2.0, 1.0, and 0.5, and 1.5, 1.0, and 0.5 for the $s$ and $p$ functions, respectively, with $n=0$. This choice gave a ground-state energy of $-2.890$ a.u.; the exact value of Pekeris is $-2.9037$ a.u.[15] The eigenvalues of $48\,^1P$ states of He were found by diagonalizing the $L=1$ rotated Hamiltonian in a basis of $6s$- and $8p$-type Slaters. As with $H^-$, the orbitals were chosen by varying $n$ and holding the orbital exponent fixed; an exponent of 1.8 was used for both the $s$ and $p$ functions.

Our results for the photoionization cross section of He are displayed in Fig. 2 along with the experimental results of Samson;[16] there is seen to be excellent agreement with experiment over the entire energy range from threshold to 100 eV. Our results also show the resonance behavior corresponding to autoionizing states of helium in the vicinity of 60 eV. This was evident from the diagonalization of the rotated Hamiltonian which produced two $^1P$ states with complex eigenvalues of $(-0.667-i0.018)$ a.u. and $(-0.586-i0.053)$ a.u. Results of Burke *et al.*[17] on the numerical solution of the close-coupling equations for $e^- - He^+$ scattering give values for these two lowest $^1P$ resonances of $-0.688$ and $-0.563$ a.u., respectively. Previous calculations on resonances using rotated coordinates have shown that resonance energies can be sensitive to variations of the

basis set and rotation angle.[8] Since our primary interest in this work was not in the characterization of resonances, our results for resonance energies and widths using one basis set and one angle should be considered preliminary.

### C. The $2\,^1S$ state of atomic helium

CI calculations were also carried out to find the first excited singlet state of $S$-symmetry for atomic helium. In these computations, an $8s$ set of Slaters was obtained by augmenting the $5s$ set of Clementi[18] by additional Slaters with exponents 0.4, 0.2, and 0.1. This calculation yielded an energy of 2.144 for the $2\,^1S$ state, compared with the Pekeris value of 2.146 a.u.[19] The basis set for the $^1P$ excited states was the Clementi $5s$ set augmented by a $7p$ set with $\alpha = 1.0$. Our results for the photoionization cross section for the $2\,^1S$ state are compared with the close-coupling results of Norcross[20] and Jacobs[21] in Fig. 3. Within the experimental uncertainty of ± 14% all three calculations are in agreement with measured values.[22]

## V. DISCUSSION

We have applied the method of rotated coordinates in calculating the photodetachment cross section of the negative hydrogen ion and the photoionization cross sections of helium in its ground and $2\,^1S$ states. Our results agree well with previous calculations and with available experiments. We have shown that the method of rotated coordinates represents an efficient and unified approach to the study of both background and resonant photoabsorption. Since the implementation of this technique only depends on the use of standard bound-state methods and matrix manipulations, it should be of considerable utility in the study of photoabsorption by heavier atoms as well as molecules.

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